

Ab initio prediction of electron and phonon transport in single-molecule junctions



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Background

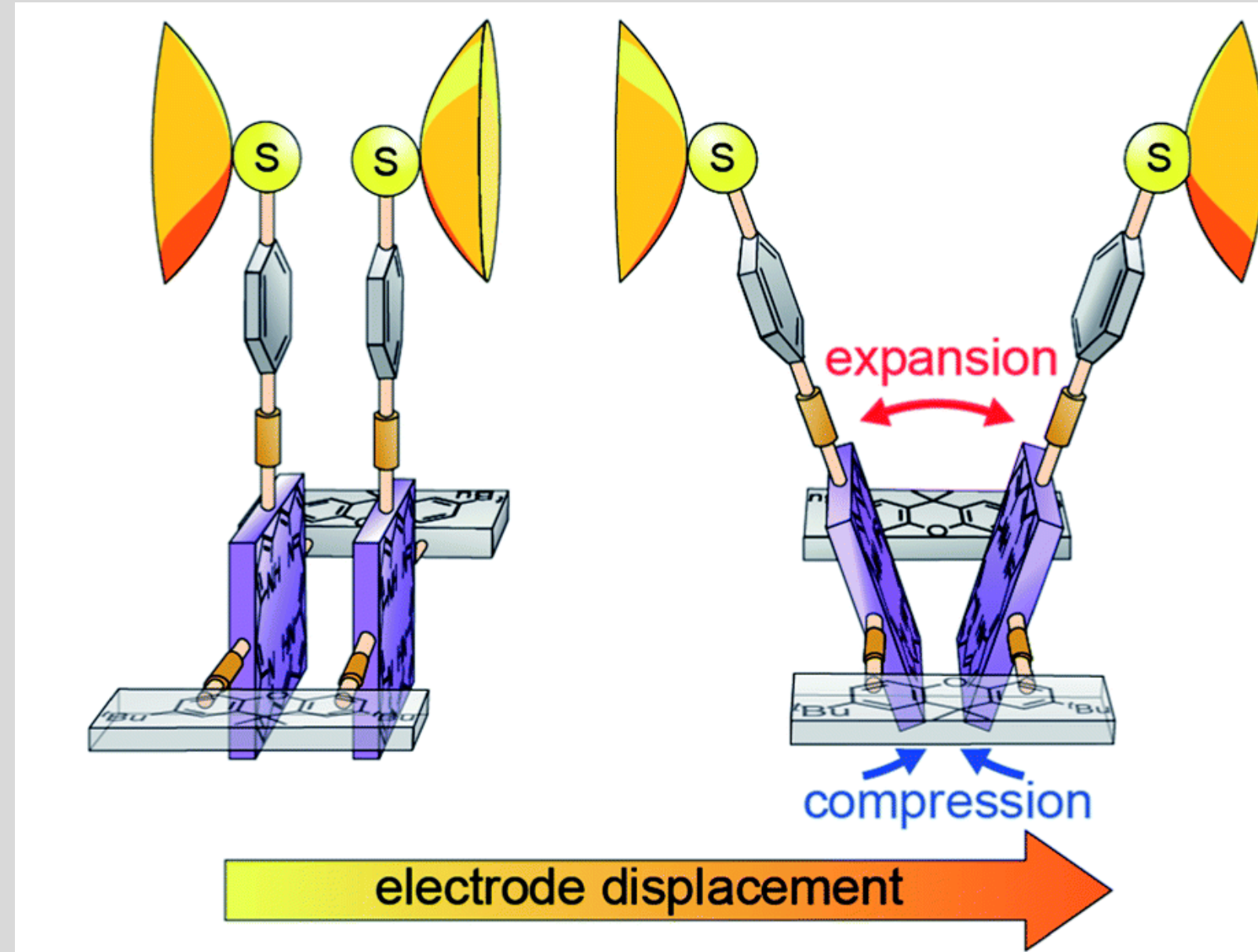


Figure taken from [7]

- Molecular Electronics:** Single molecules serve as electronic components when contacted by macroscopic electrodes
- Circuit Design via Chemistry:** Aiming at creating functional circuits through precise chemical design
- Fundamental research on transport mechanisms:** Single-molecule junctions are ideal test platforms
- New Functionalities:** Transport properties influenced by quantum effects allow for novel applications

Electron transport description

- Landauer formalism:** Transmission $\tau(E)$ calculated by

$$\tau(E) = \text{Tr} [\Gamma_L^r(E) G_C^r(E) \Gamma_R^r(E) G_C^a(E)]$$

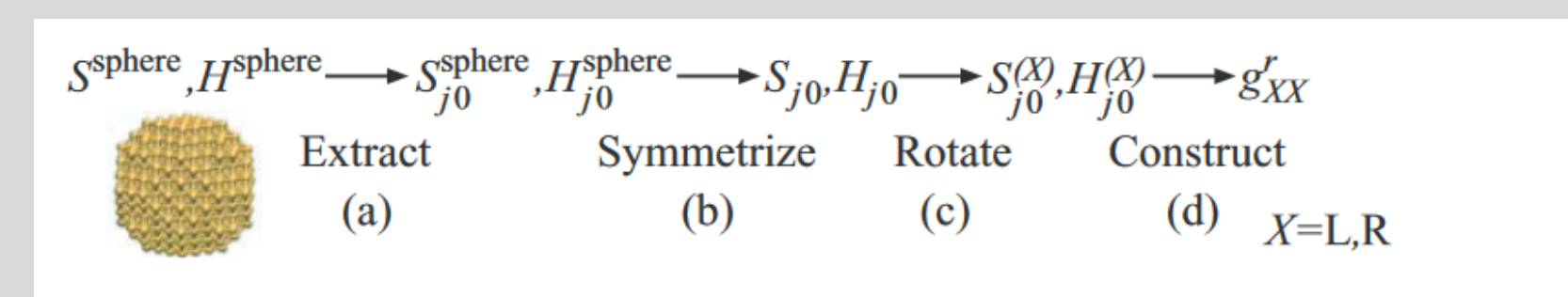
$$G_C^r(E) = [E S_C - H_C - \Sigma_L^r(E) - \Sigma_R^r(E)]^{-1}$$

$$\Sigma_X^r = (H_{CX} - E S_{CX}) g_X(E) (H_{XC} - E S_{XC})$$

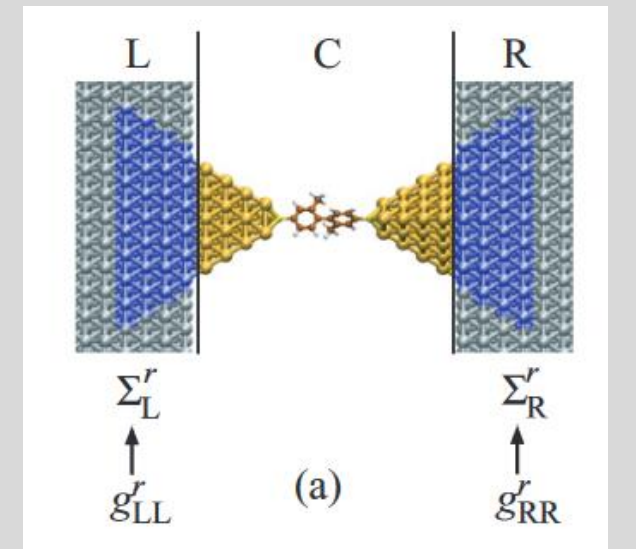
$$\Gamma_X(E) = -2\text{Im} [\Sigma_X^r(E)]$$

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- Cluster-based approach:** [4]

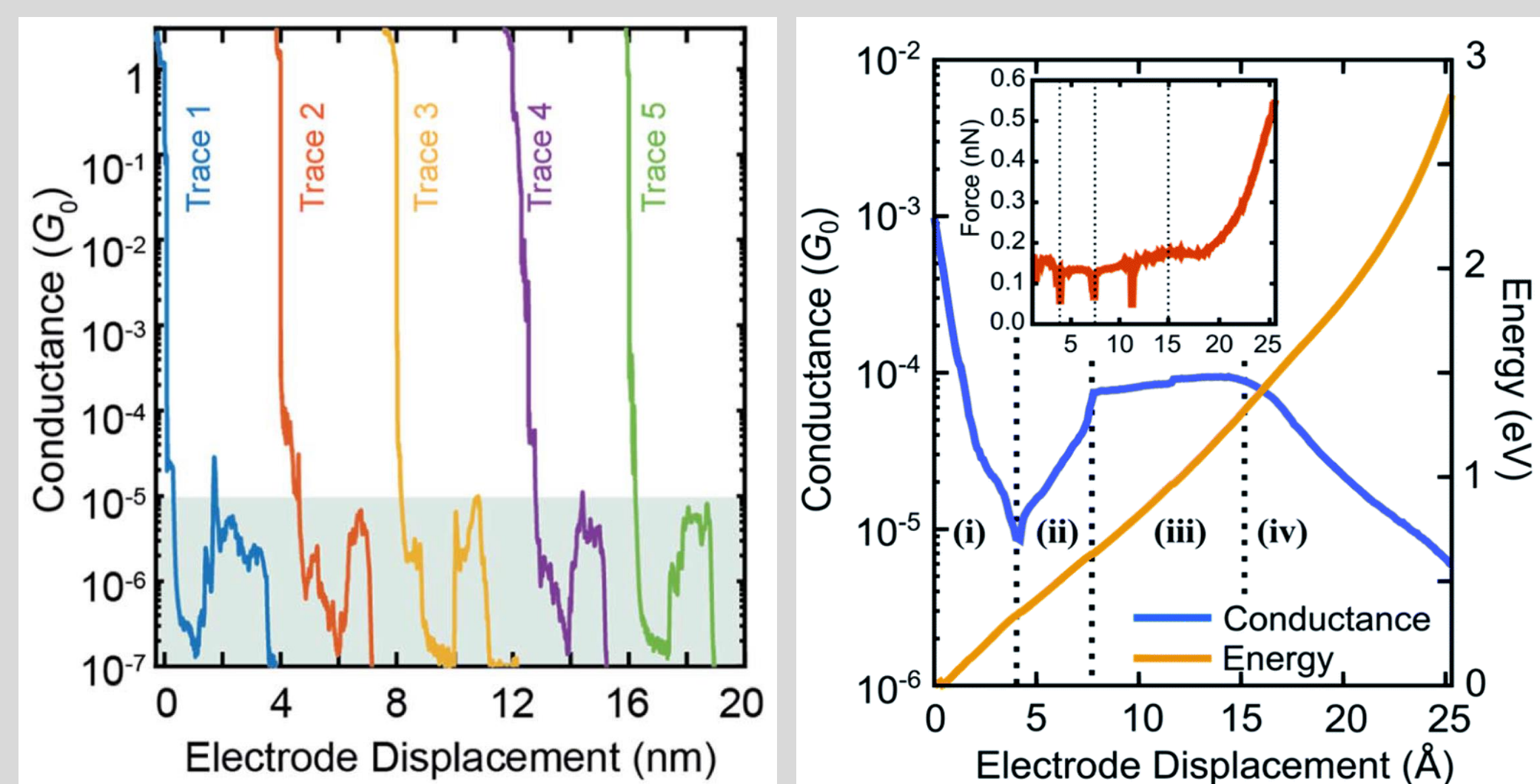


Figures taken from [4]



- Derived electronic properties:** Conductance and thermopower

Electronic transport



Figures taken from [7]

- Good agreement between experimental data and theoretical prediction
- Rigorously tested and validated through an extensive record of collaborative experimental research [1,2,6-10]

Insight into transport mechanisms

- Decomposition into transmission eigenchannels and corresponding wave functions:

$$G = G_0 \sum_n \tau_n(E_F)$$

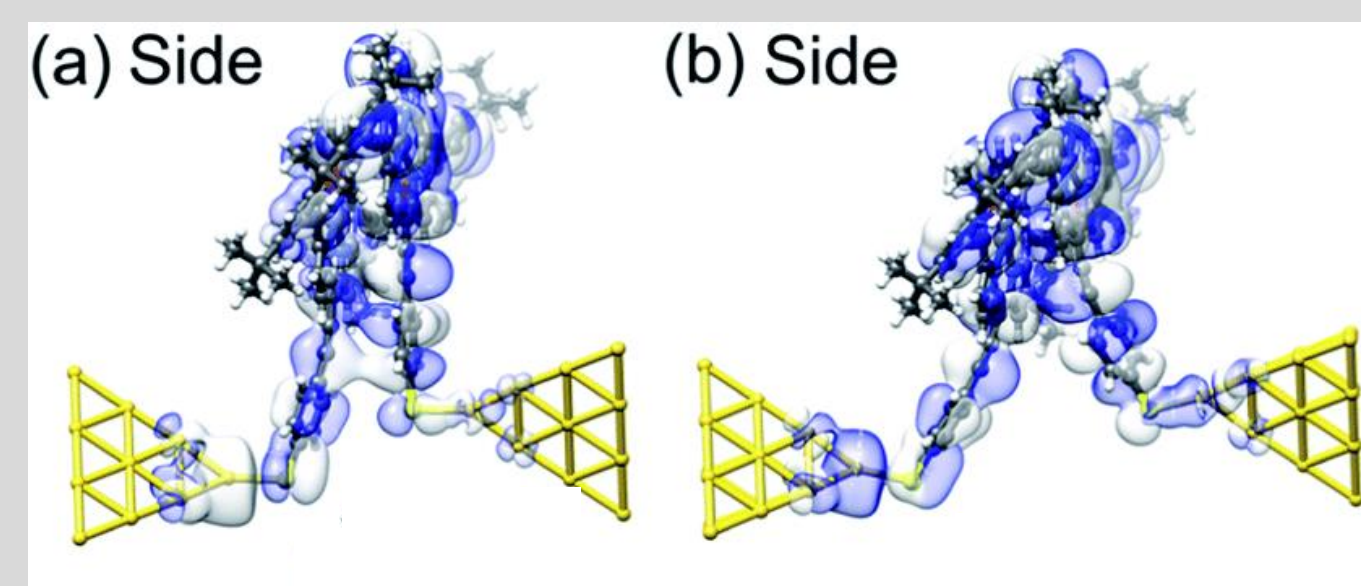


Figure taken from [7]

- Analysis shows crossover from through-space to through-bond transport

Corrections to DFT level alignment [6,7,8]

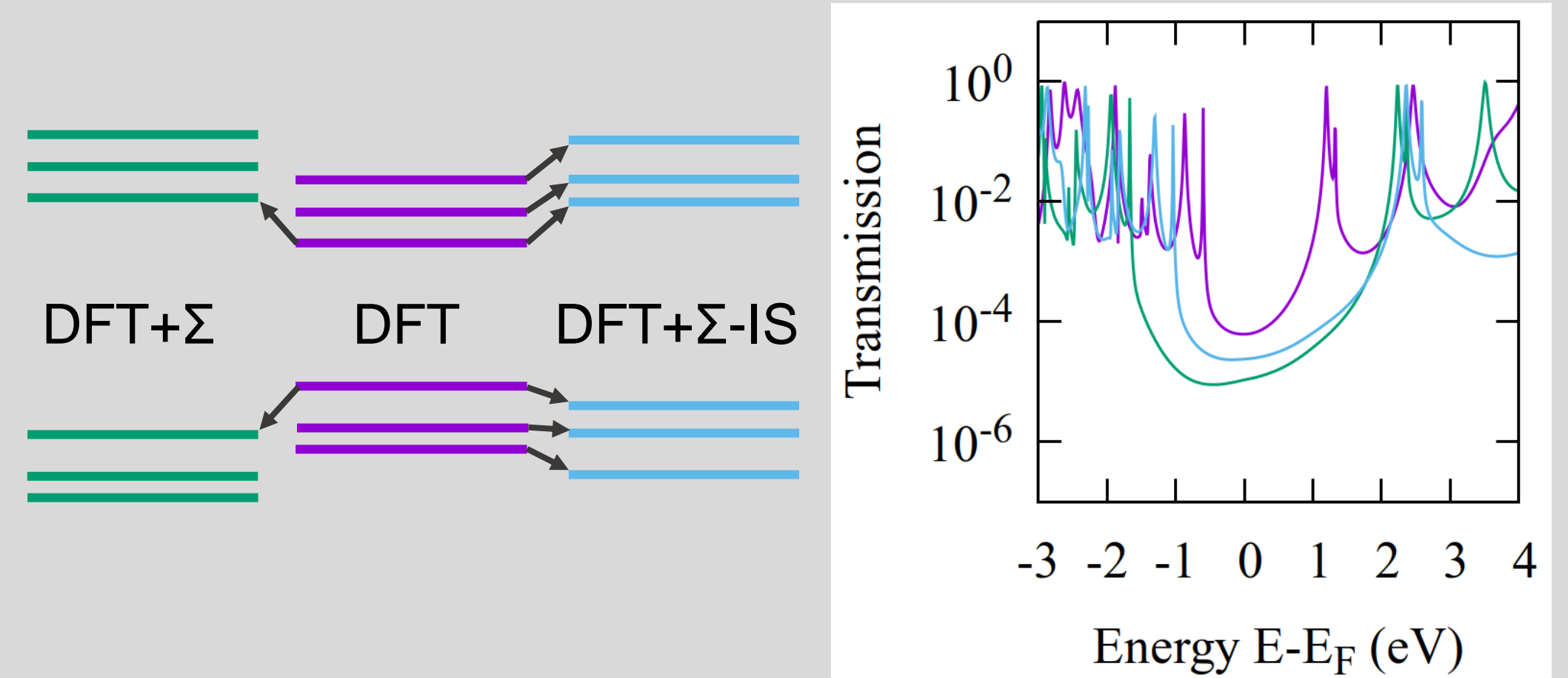


Figure taken from [8]

DFT+Σ: Uniform shift

$$\Sigma^{\text{vrt}} = (-EA - \epsilon_L) - \Delta_{\text{LUMO}}$$

$$\Sigma^{\text{occ}} = (-IP - \epsilon_H) - \Delta_{\text{HOMO}}$$

molecular gap correction image charge correction

DFT+S-IS: Individual shift

$$\Sigma^{\text{vrt}} = (\epsilon_i^{\text{G}_0 W_0} - \epsilon_i^{\text{DFT}}) - \Delta_i$$

$$\Sigma_i^{\text{occ}} = (\epsilon_i^{\text{G}_0 W_0} + \epsilon_i^{\text{DFT}}) - \Delta_i$$

molecular gap correction image charge correction

Phononic Transport

- Relevance:** Measurements of the thermal conductance of single-molecule junctions have only recently become possible [2]
- Theoretical modeling:** Landauer formalism

$$\tau_{\text{ph}}(E) = \text{Tr} [\Lambda_L^r(E) D_C^r(E) \Lambda_R^r(E) D_C^a(E)]$$

$$D_C^r(E) = [(E + i\eta)^2 - K_C - \Pi_L^r(E) - \Pi_R^r(E)]^{-1}$$

$$\kappa_{\text{ph}}(T) = \frac{1}{h} \int_0^\infty dE E \tau_{\text{ph}}(E) \frac{\partial n(E, T)}{\partial T}$$

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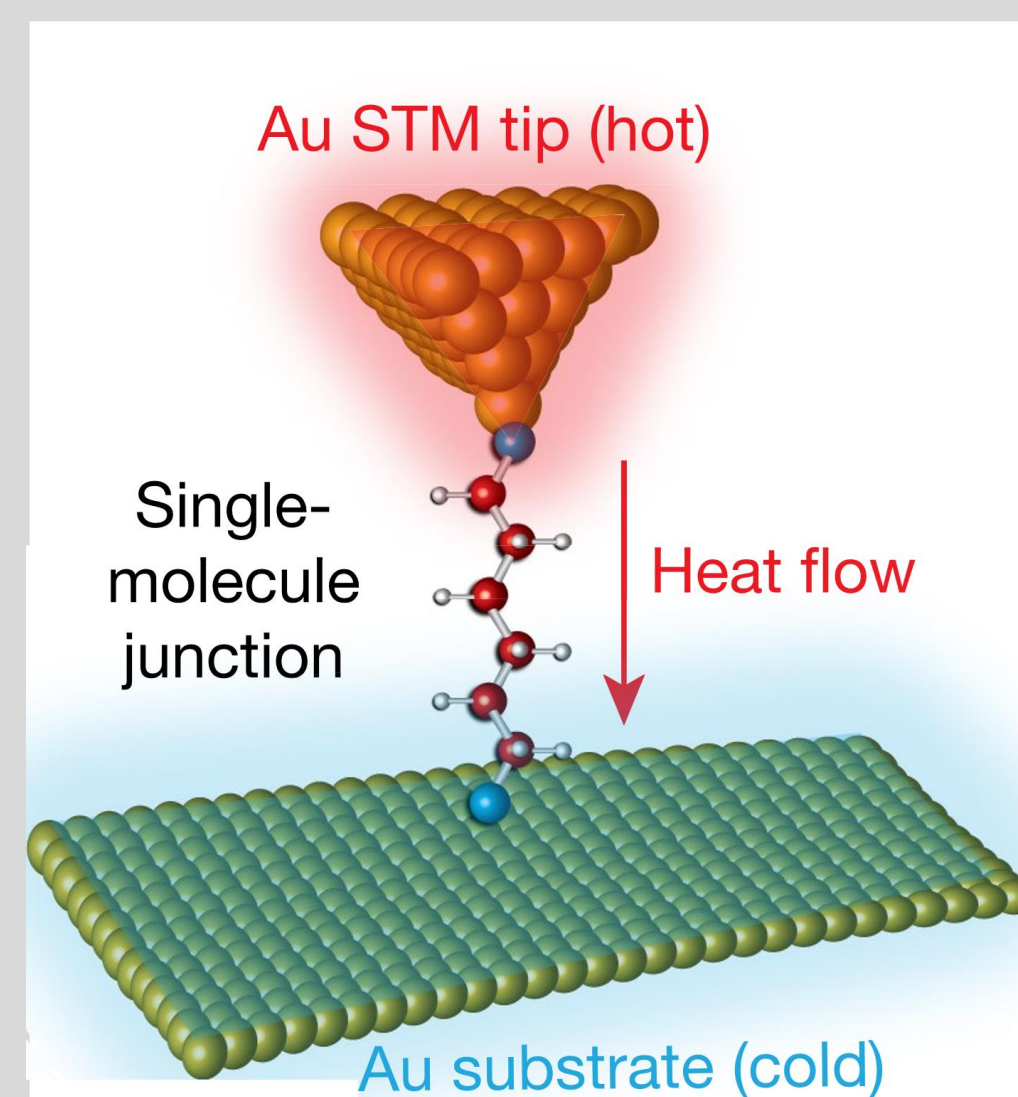
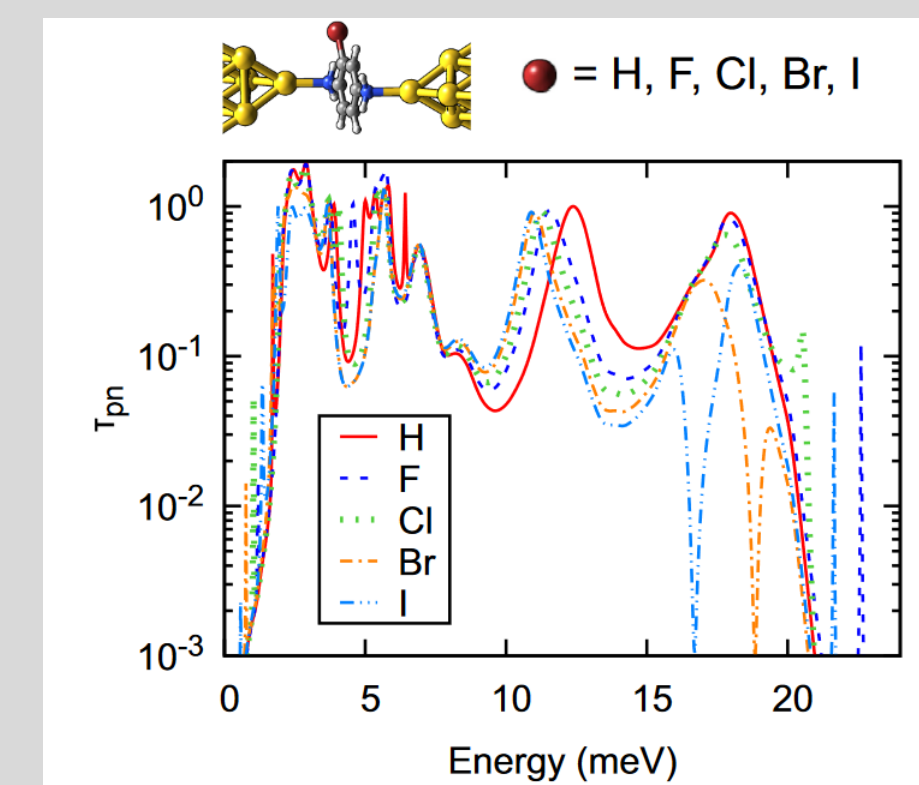
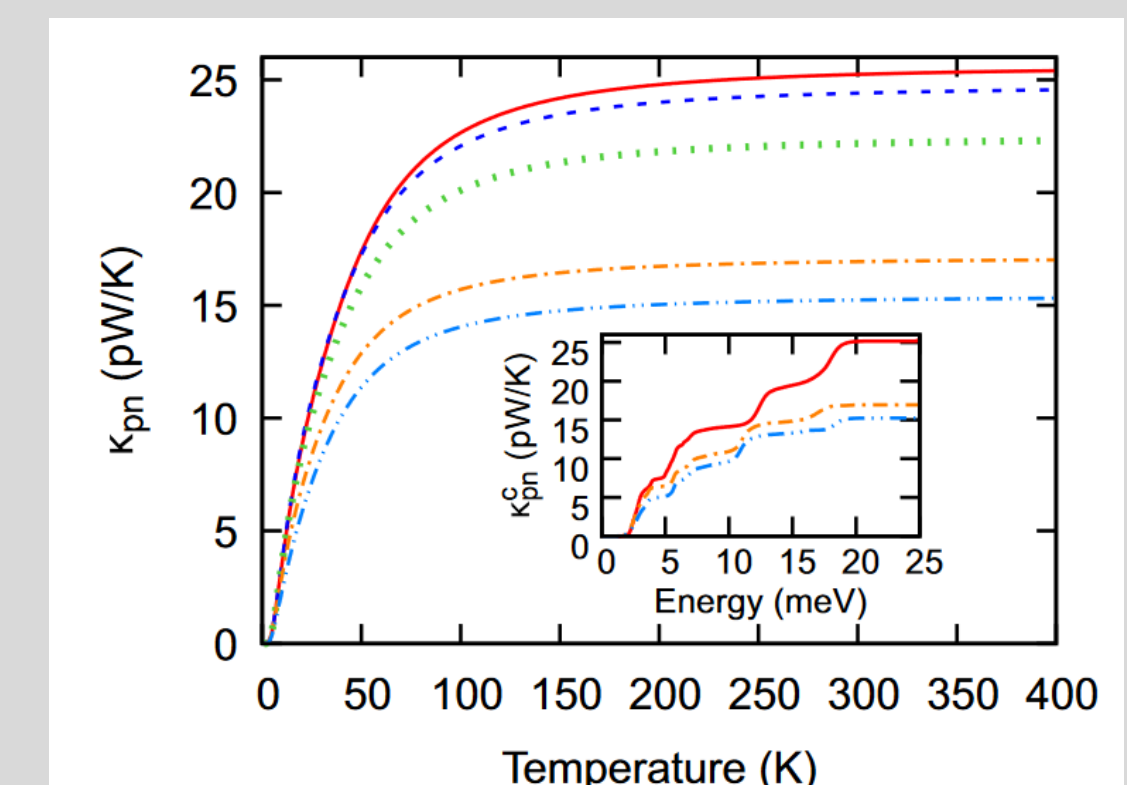


Figure taken from [2]



Figures taken from [11]



- Lattice contribution is the most relevant part of the thermal conductance for electrically rather insulating molecules
- Tools for calculation of phonon transmission and eigenchannel analysis available

Further computational tools and applications

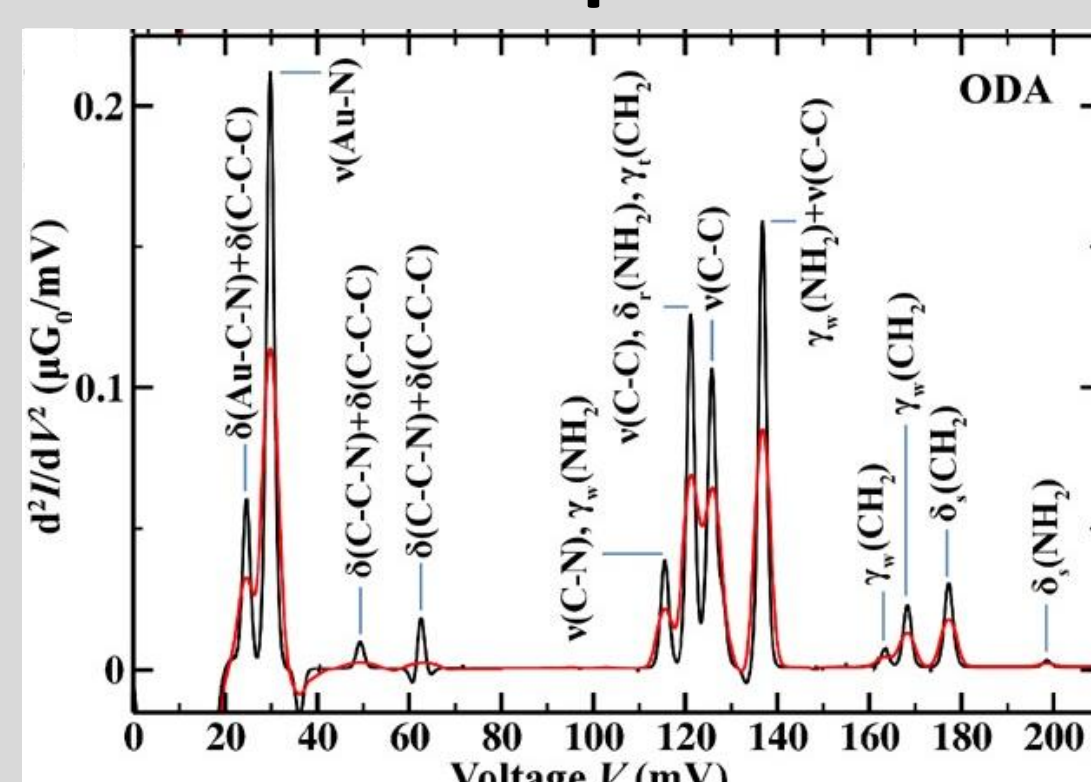


Figure taken from [13]

Inelastic electron tunneling (IET)

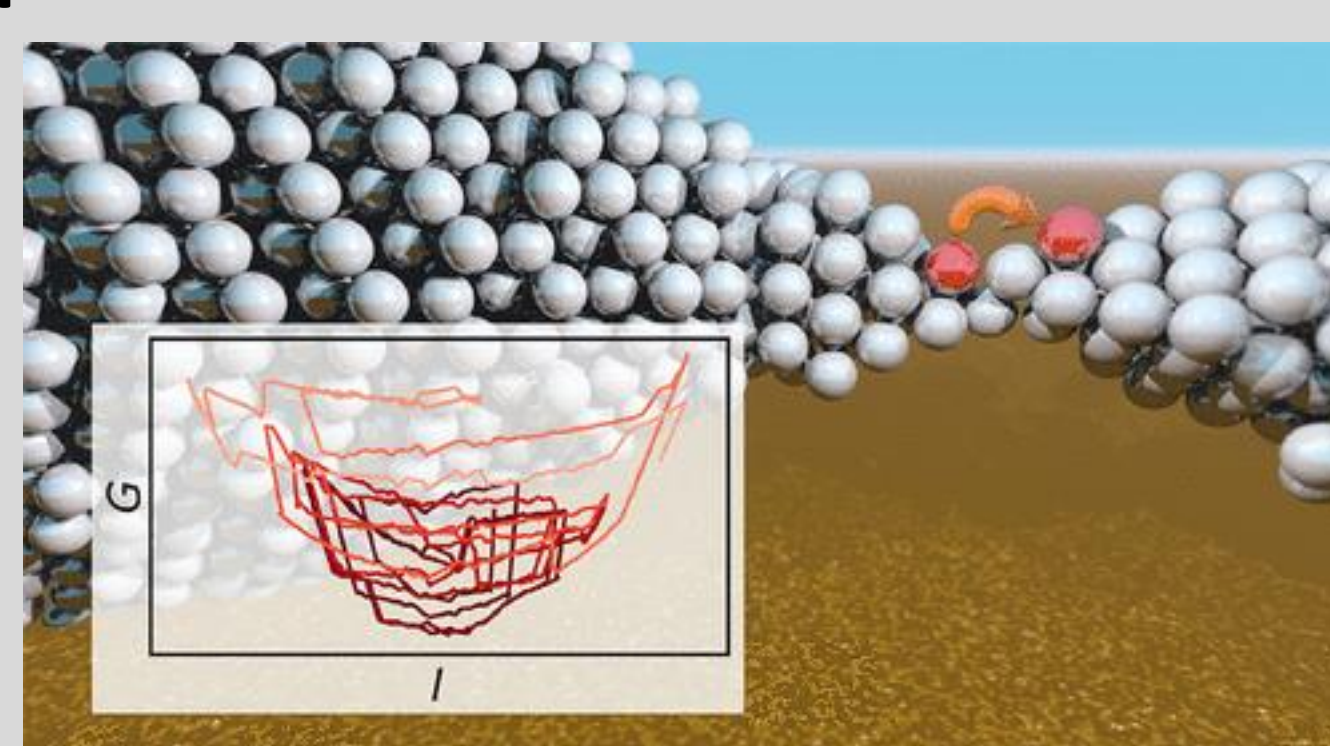


Figure taken from [14]

Current induced forces

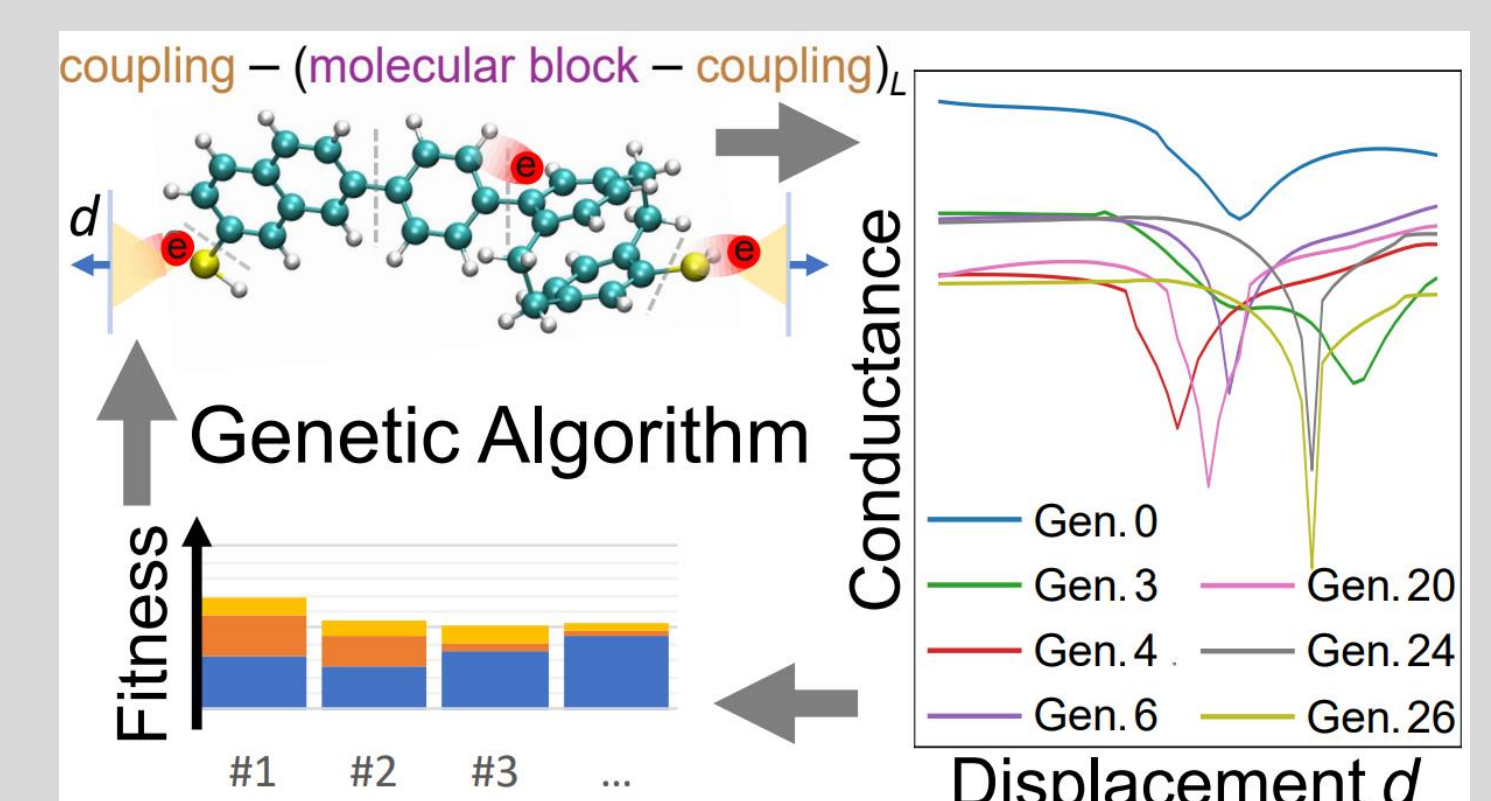


Figure taken from [15]

Molecular design: Tailor transport properties

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